



(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
04.06.1997 Bulletin 1997/23

(51) Int Cl.⁶: **C07D 291/06, B27K 3/34,**
C07D 419/04

(21) Application number: **94926617.5**

(86) International application number:
PCT/US94/09702

(22) Date of filing: **24.08.1994**

(87) International publication number:
WO 95/06043 (02.03.1995 Gazette 1995/10)

(54) **WOOD PRESERVATIVE OXATHIAZINES**
OXATHIAZINE HOLZSCHUTZMITTEL
OXATHIAZINES DE PROTECTION DU BOIS

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IE IT LI LU MC NL
PT SE

(30) Priority: **24.08.1993 US 111386**

(43) Date of publication of application:
12.06.1996 Bulletin 1996/24

(73) Proprietors:
• **UNIROYAL CHEMICAL COMPANY, Inc.**
Middlebury Connecticut 06749 (US)
• **UNIROYAL CHEMICAL LTD./UNIROYAL**
CHEMICAL LTEE
Elmira Ontario N3B 3A3 (CA)

(72) Inventors:
• **DAVIS, Robert, A.**
Cheshire, CT 06410 (US)
• **VALCKE, Alex, R., A.**
B-2275 Wechelderzande (BE)
• **BROUWER, Walter, G.**
Guelph, Ontario N1G 2X2 (CA)

(74) Representative: **Spott, Gottfried, Dr.**
Patentanwälte
Spott, Weinmiller & Partner
Sendlinger-Tor-Platz 11
80336 München (DE)

(56) References cited:
EP-A- 0 104 940 **EP-A- 0 363 316**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

BACKGROUND OF THE INVENTION**1. Field of the Invention**

The present invention relates to a process for preserving wood and composite wood materials from wood damaging organisms, and compositions useful in such process.

This invention more specifically is directed to a class of 3-aryl-5,6-dihydro-1,4,2-oxathiazines and their oxides which are useful against such wood damaging organisms as bacteria, yeasts, and fungi.

This invention is also directed to novel 3-aryl-5,6-dihydro-1,4,2-oxathiazines and their oxides which are useful against such wood damaging organisms as bacteria, yeasts, and fungi.

2. Description of Related Art

The preservation of wood is a subject of great economic importance. For most purposes, untreated wood is entirely unsatisfactory. It will twist, warp, and crack as it dries; it cannot easily be glued or finished, and it is subject to attack of fungi and/or insects. Properly prepared and preserved wood possesses strength and incompressibility while being flexible.

U.S. Patent 4,569,690 refers to various 3-aryl-5, 6-dihydro-1,4,2-oxathiazines and their oxides said to be useful as herbicides, plant fungicides, plant dessicants and defoliants. No mention is made of preserving wood materials from damaging organisms.

Chemical Abstracts 103(1):2144u refers to fungicides containing phenyl-alpha-chloroacetamides said to be effective in industrial environments including paints, metal cutting fluids, and to prevent the growth of cellulose degrading fungus on treated wood.

Chemical Abstracts 102(16):133786g refers to resistance to biological attack in wood treated with epoxides. U.S. Patent 4,562,185 refers to 1-oxo-3-azacyclopentane derivatives said to be useful as pesticides, especially systemic insecticides, effective against acarids and nematodes and showing residual activity on wood and clay.

U.S. Patent 4,067,862 refers to a process for modification of polymeric materials with a nitrile sulfide. The modified polymers are said to have uses including decorative or protective coatings for wood.

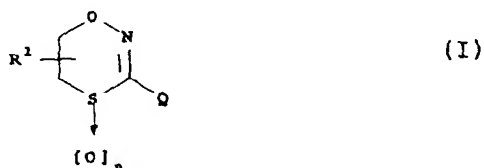
World Patents Index 67-05105G/00 refers to fungicidal 2-mono substituted amino 1-azacycloalkene-1 compounds, said to have fungicidal activity in both plants and other organic materials including wood.

U.S. Patent 4,977,186 refers to wood preservative and soil treatment compositions containing carbamates.

European Patent Application 0 363 316 describes certain 3,5-dihalogeno-1,2,6-thiadiazin-4-ones useful as biocides for protecting industrial materials and water systems.

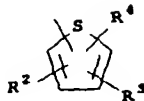
SUMMARY OF THE INVENTION

This invention relates to a compound of the formula



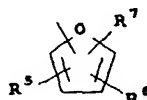
wherein n is 0, 1 or 2; R¹ is hydrogen, C₁-C₄ linear or branched alkyl, or benzyl; and Q is:

(a)



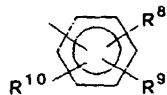
wherein R^2 , R^3 and R^4 are, individually, hydrogen, alkyl, alkoxy, alkylthio, alkoxycarbonyl, halogen, trihalomethyl, cyano, acetyl, formyl, benzoyl, nitro, alkoxyaminomethyl, phenyl, or phenylaminocarbonyl, wherein the alkyl or alkoxy moieties are all C_1 - C_4 , linear or branched, with the proviso that at least one of R^2 , R^3 or R^4 must be other than hydrogen;

(b)



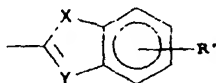
wherein R^5 , R^6 and R^7 are, individually, hydrogen, C_1 - C_4 alkoxy, C_1 - C_4 alkylthio, halogen, trihalomethyl, cyano, acetyl, formyl, benzoyl, nitro, phenyl, or phenylaminocarbonyl, with the proviso that at least one of R^5 , R^6 or R^7 must be other than hydrogen;

(c)



wherein R^8 , R^9 and R^{10} are, individually, hydroxyl, halo, C_1 - C_{12} alkyl, C_5 - C_6 cycloalkyl, trihalomethyl, phenyl, C_1 - C_5 alkoxy, C_1 - C_5 alkylthio, tetrahydropyranyloxy, phenoxy, $(C_1$ - C_5 alkyl)carbonyl, phenylcarbonyl, C_1 - C_4 alkylsulfinyl, C_1 - C_4 alkylsulfonyl, carboxy or its alkali metal salt, $(C_1$ - C_4 alkoxy) carbonyl, $(C_1$ - C_4 alkyl) aminocarbonyl, phenylaminocarbonyl, tolylaminocarbonyl, morpholinocarbonyl, amino, nitro, cyano, dioxolanyl, or $(C_1$ - C_4 alkoxy)iminomethyl; or

(d)

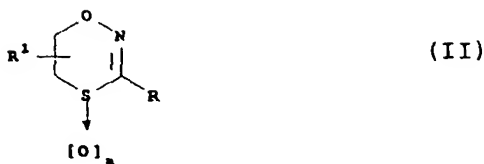


wherein X is oxygen or sulfur; Y is nitrogen, $-CH-$, or $-C(C_1-C_4 \text{ alkoxy})-$; and R^* is hydrogen or C_1 - C_4 alkyl.

The compounds of the present invention are useful for the long-term preservation of wood and composite wood materials against wood damaging and wood destroying materials.

The present invention also provides methods useful for the long-term preservation of wood and composite wood materials against wood damaging and wood destroying materials. For the purpose of this invention, a composite wood material is any product made from wood, including, but not limited to, plywood, pressed wood, chipboard, particleboard, wafer board, wood laminated material and the like.

In accordance with the present methods, a wood material is preserved by treatment with a fungicidally or bactericidally effective amount of an active agent represented by the formula below



wherein n is 0, 1 or 2; R¹ is hydrogen, C₁-C₄ linear or branched alkyl, or benzyl; and

R is:

(a) phenyl; naphthyl; phenyl substituted with 1-3 of the following substituents:

hydroxyl, halo, C₁-C₁₂ alkyl, C₅-C₆ cycloalkyl, trihalomethyl, phenyl, C₁-C₅ alkoxy, C₁-C₅ alkylthio, tetrahydro-pyranlyloxy, phenoxy, (C₁-C₄ alkyl) carbonyl, phenylcarbonyl, C₁-C₄ alkylsulfinyl, C₁-C₄ alkylsulfonyl, carboxy or its alkali metal salt, (C₁-C₄ alkoxy) carbonyl, (C₁-C₄ alkyl) aminocarbonyl, phenylaminocarbonyl, tolylaminocarbonyl, mor-

pholinocarbonyl, amino, nitro, cyano, dioxolanyl, or (C₁-C₄ alkoxy)iminomethyl;

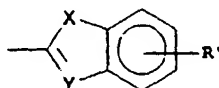
pyridinyl; thienyl, preferably when n is not 2; furanyl; thienyl or furanyl substituted with 1 to 3 of the following groups:

alkyl, alkoxy, alkylthio, alkoxy carbonyl, halogen, trihalomethyl, cyano, acetyl, benzoyl, nitro,

formyl, alkoxyaminomethyl, phenyl, or phenylaminocarbonyl, wherein the alkyl or alkoxy moiety is C₁-C₄, linear or branched;

or thienyl substituted with 1 to 3 alkoxyaminomethyl, wherein the alkoxy moiety is C₁-C₄, linear or branched; or

(b)



wherein X is oxygen or sulfur; Y is nitrogen, -CH-, or -C(C₁-C₄ alkoxy)-; and R* is hydrogen or C₁-C₄ alkyl.

In further accordance with the present invention, there is provided a composition comprising a) a wood preservative amount of a compound of formula I, and b) a suitable carrier.

DETAILED DESCRIPTION OF THE INVENTION

A preferred embodiment of the compounds of this invention are those compounds of formula I wherein R¹ is hydrogen or C₁-C₄ alkyl; n is 1 or 2; R², R³ and R⁴ are, individually, hydrogen, C₁-C₄ alkyl, halo, (C₁-C₄ alkoxy)-carbonyl, or cyano, with the proviso that at least one of R², R³ and R⁴ must be other than hydrogen; R⁵, R⁶ and R⁷ are, individually, hydrogen, halo or cyano, with the proviso that at least one of R⁵, R⁶ and R⁷ must be other than hydrogen; R⁸, R⁹ and R¹⁰ are C₁-C₄ alkyl, C₁-C₄ alkoxy, nitro, halo, trihalomethyl, or (C₁-C₄ alkoxy)-carbonyl; X is sulfur; and R* is hydrogen.

More preferred are those compounds of formula I wherein R¹ is hydrogen; n is 1 or 2; R², R³ and R⁴ are, individually, hydrogen, methyl, ethyl, bromo, chloro, ethyl carboxylate, or cyano, with the proviso that at least one of R², R³ and R⁴ must be other than hydrogen; R⁵, R⁶ and R⁷ are, individually, hydrogen, bromo, chloro or cyano, with the proviso that at least one of R⁵, R⁶ and R⁷ must be other than hydrogen; R⁸, R⁹ and R¹⁰ are methyl, ethyl, nitro, fluoro, chloro, or trifluoromethyl.

In a preferred embodiment of the method of the present invention, the compounds of structure II are substituted with R¹ being hydrogen, n being one or two, and R has one or 2 of the following values:

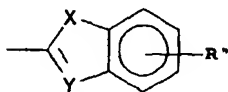
phenyl, (C₁-C₆ alkyl)phenyl, halophenyl, dihalophenyl, biphenyl, (C₁-C₅ alkoxy)phenyl, trihalomethylphenyl, nitrophenyl, phenyl substituted with (C₁-C₄ alkoxy)carbonyl, furanyl, furanyl substituted by ethyl carboxylate, cyano, chlorine, or bromine, thienyl, thienyl substituted with ethyl carboxylate, cyano, chlorine, or bromine, or (C₁-C₆ alkyl) nitrophenyl.

In a still further preferred embodiment of the method of this invention, R¹ is hydrogen, n is one or two, and R is represented by:

4-chlorophenyl, 3-nitrophenyl, 3,4-dichlorophenyl,
3-fluorophenyl, 2-thienyl, 4-methylphenyl,
3-trifluoromethylphenyl, 3-ethanonephenyl,
3,5-dichlorophenyl, 4-trifluoromethylphenyl,

3-methyl-4-nitrophenyl.

In another preferred embodiment of the method of this invention, R¹ is hydrogen, and R is



wherein X is sulfur, Y is nitrogen or -CH-, and R* is hydrogen.

The compounds of formula I and II can be prepared utilizing the procedures described in U.S. Patent 4,569,690, or the procedures described in Examples 1-8 below. That patent discloses detailed examples of the synthesis of several 3-aryl-5,6-dihydro-1,4,2-oxathiazines and their oxides by two methods: one utilizing aromatic aldehydes as starting materials and one using arylcarbodithioate esters. Either method is viable and may be understood by one skilled in the art of organic chemical synthesis.

The compositions of this invention include a suitable carrier. Generally, the carrier may be a liquid vehicle for dissolving or suspending the active wood preservative ingredient. The vehicle typically contains at least one of a diluent, an emulsifier, and a wetting agent.

In addition, the carrier may also include other adjuvants conventionally employed in wood preserving compositions, such as organic binding agents, additional fungicides, insecticides, auxiliary solvents, processing additives, fixatives, plasticizers, UV-stabilizers or stability enhancers, water soluble or water insoluble dyes, color pigments, siccatives, corrosion inhibitors, antisetling agents, anti-skinning agents, and the like.

The wood preservative composition is typically supplied as a preparation with the active ingredients dissolved or dispersed in a liquid vehicle or carrier material, such that the active chemical ingredient(s) comprise from about 0.001% by weight up to about 10% by weight of the total composition. More generally, the active fungicidal or bactericidal ingredients will comprise from about 0.1 to 5% by weight, and most often from about 1 to about 5% by weight. For most wood preservative applications, the liquid vehicle can constitute as little as 5% by weight of the preparation. The composition of the present invention can be provided as a ready for use product in the form of aqueous solutions and dispersions, emulsions, aerosol preparations and the like or as a concentrate. The concentrate can be used as is, for example, as an additive for plywood glues, or can be diluted prior to use with additional solvent or suspending agents.

The liquid vehicle is not a critical aspect of the present invention and any liquid that does not interfere with the bactericidal and fungicidal activities of the active ingredients and which is compatible with wood preserving applications potentially can be used in the present invention. Suitable diluents for the liquid vehicle include water and organic solvents including aromatic hydrocarbons such as xylene, toluene, high aromatic petroleum distillates such as solvent naphtha, distilled tar oil and mixtures thereof, alcohols such as butanol, octanol, and glycols, vegetable and mineral oils, ketones such as acetone, petroleum fractions such as mineral spirits and kerosene and the like.

The diluent of the liquid vehicle generally comprises an organic solvent or solvent mixture. The liquid vehicle may contain at least one polar solvent, such as water, in admixture with an oily or oil-like low volatility organic solvent, such as the mixture of aromatic and aliphatic solvents found in white spirits, also commonly called mineral spirits.

Oily or oil-like or organic solvents useful in the present invention preferably have a flash point above 28°C and a boiling range, at atmospheric pressure, between about 130°C to 250°C while low-volatility organic solvents preferably have a flash point above about 55°C and a boiling range, at atmospheric pressure, between about 180°C to 350°C. The liquid vehicle is selected to enhance penetration of the active ingredients into the wood or wood product being treated.

An aerosol preparation according to the invention is obtained in the usual manner by incorporating the active ingredients dissolved or suspended in a suitable solvent, in a volatile liquid suitable for use as a propellant, for example, the mixture of chlorine and fluorine derivatives of methane and ethane commercially available under the FREON trademark, or compressed air.

The balance of the composition may include additional ingredients known to be useful in wood preservatives and related products. Such ingredients include organic binding agents, such as alkyd resins; fixatives such as carboxymethylcellulose, polyvinyl alcohol, paraffin and the like; co-solvents, such as ethylglycol acetate and methoxypropyl acetate; and plasticizers such as benzoic acid esters and phthalates, for example, dibutyl phthalate, dioctyl phthalate, and didecyl phthalate. Optionally, dyes, color pigments, corrosion inhibitors, chemical stabilizers or dryers such as cobalt octate and cobalt naphthenate also may be included depending on specific applications and user preference.

The organic binding agent can be a chemically drying organic binder-forming polymer or a physically drying organic binder forming solids by solvent evaporation. Alkyd resins are a suitable class of organic binding agents; others will

be recognized by those skilled in the art. The organic binding agents may themselves be supplied in a liquid vehicle, and in that case the amounts referred to herein for the organic binder are on a solids basis.

As mentioned above, such additional ingredients may include additional fungicides and insecticides. Suitable additional fungicides would be apparent to one skilled in the art, and will vary according to application. Examples include those fungicides known to have wood preservation uses, such as azaconazole, dichlofluanid, acypetacs, propiconazole, imazalil, cyproconazole, hexaconazole, IPBC, isothiazolone, tolylfluanid, chlorotalonil, benzimidazoles, Cu-oxides and Cu-HDO. Suitable insecticides would also be apparent depending upon application, and could include, for example, chlorpyrifos, cypermethrin, fenvalerate, isofenphos, permethrin, silafluofen, deltamethrin, cyfluthrin and imidachloprid. Such additional ingredients are not essential to the practice of the present invention but are included in particular formulations to optimize overall effectiveness and ease of application. The specific examples of suitable constituents for a wood preservative preparation as enumerated above are not meant to be limiting and a wide variety of other possible ingredients will be recognized to one skilled in the art. Similarly, the quantity of such ingredients in any formulation is not critical and can be used in an amount conventionally employed for products designed to be used in wood preserving applications. Normally, the totally formulated compositions may contain from about 0.1% to 95% by weight, and more usually from about 1% to 50% by weight of these additional ingredients on a total solids basis.

The wood preservative composition can be applied by any of the techniques known in the art including brushing, spraying, dipping, and the like. Generally, to obtain an effective treatment, it should be efficient to apply between about 0.05 to 0.4 kilogram of the composition per square meter of wood surface area to be treated, which is equivalent to about 0.01 to 0.08 pound per square foot. An amount of about 0.1 to 0.2 kg/m², or about 0.02 to 0.04 pound/square foot, is more typical.

The active ingredient may also be applied in the wood by methods known in the art. Such methods include vacuum pressure impregnation, injection and diffusion. Suitable dose ranges for these methods include from about 0.01 to about 6.0 Kg/m³ and preferably from about 0.5 to about 6 kg/m³, and more preferably from about 0.5 to about 1.5 kg/m³ of active ingredient in the treated wood.

The composition of the present invention can be prepared by mixing the various ingredients at a temperature at which they are not adversely affected, which usually will be from about -5°C to 80°C, preferably at a temperature of from about 10°C to 45°C, and at a pressure of 6x10⁴ Pa to 12x10⁴ Pa (450 mm Hg to 900 mm Hg), preferably at about 8.7x10⁴ Pa to 11.3x10⁴ Pa (650 mm Hg to 850 mm Hg). Preparation conditions are not critical. Equipment and methods conventionally employed in the manufacture of coating compositions may be advantageously employed.

The following examples are presented for illustrative purposes and are not intended to limiting the scope of this invention in any manner.

The compounds listed in Table 1 were prepared utilizing the procedures described in U.S. Patent 4,569,690. The compounds listed in Tables 2, 3 and 4 were prepared utilizing the procedures described in Examples 1-9 below.

EXAMPLES

Example 1

1,4,2-Oxathiazine,3-(5-chloro-2-thienyl)-5,6-dihydro(Compound #59)

Methyl 5-chloro-2-thiophenecarbodithioate (61.4g, 0.29 mol) was suspended in methanol (400 ml) with finely powdered hydroxylamine hydrochloride (25g). With stirring, triethylamine (50 ml) in methanol (50 ml) was added dropwise to the suspension, to produce a reaction mixture. During this addition, the reaction mixture was cooled to 5°C. Stirring of the reaction mixture was continued until an orange (from red) color developed in the reaction mixture. Additional triethylamine (100 ml) was then added at once, followed by 1,2-dibromoethane (20 ml). The resultant reaction mixture was then stirred overnight at ambient temperature. The reaction mixture was then refluxed with removal of solvent until a precipitate appeared. The reaction mixture was then cooled and water was added. The reaction mixture was then filtered and the solid collected on the filter was recrystallized from ethanol to produce 3-(5-chloro-2-thienyl)-5,6-dihydro-1,4,2-oxathiazine (mp 74-77°C, 21.4g. Found C 38.5, H 2.94, N 6.45, C₇H₆ClNOS₂ requires C 38.27, H 2.73, N 6.38)

Example 2

3-(5-Chloro-2-thienyl)-5,6-dihydro-1,4,2-oxathiazine-4,4-dioxide (Compound #61)

3-(5-Chloro-2-thienyl)-5,6-dihydro-1,4,2-oxathiazine (12g, 0.055 mol) prepared in Example 1, in methylene chloride (50 ml) and anhydrous magnesium sulphate (10g) in suspension, was stirred while *m*-chloroperoxybenzoic acid (34g, 50-60% material) in methylene chloride (250 ml), was added dropwise, to prepare a reaction mixture. The reaction mixture was allowed to warm to 30°C and after the dropwise addition was externally heated to 35°C for 10 hours by

which time a negative starch/KI test was obtained. Unwanted m-chlorobenzoic acid was then removed from the reaction mixture by extraction with aqueous sodium bicarbonate. The remaining reaction mixture was washed with water, dried (MgSO₄) and evaporated to dryness. The resultant residue was chromatographed on 500g silica gel eluting with methylene chloride, to produce 3-(5-chloro-2-thienyl)-5,6-dihydro-1,4,2-oxathiazine-4,4-dioxide (mp 113-114°C, 14.3g, Found: C 33.27, H 2.33, N 5.55; C₇H₆ClNO₃S₂ requires C 33.40, H 2.39, N 5.57).

Example 3

Synthesis of 3-(5-chloro-2-thienyl)-5,6-dihydro-1,4,2-oxathiazine-4-oxide (Compound #60)

3-(5-Chloro-2-thienyl)-5,6-dihydro-1,4,2-oxathiazine (12.4g, 0.056 mol) prepared in Example 1, in methylene chloride (50 ml), was stirred while m-chloroperoxybenzoic acid (16.2g) in methylene chloride (250 ml), was added dropwise, to prepare a reaction mixture. The reaction mixture was allowed to warm to 30°C and after the dropwise addition was externally heated to 35°C for 10 hours by which time a negative starch/KI test was obtained. Unwanted m-chlorobenzoic acid was then removed from the reaction mixture by extraction with aqueous sodium bicarbonate. The remaining reaction mixture was washed with water, dried (MgSO₄) and evaporated to dryness. The resultant residue was chromatographed on 500g silica gel eluting with methylene chloride, to produce 3-(5-chloro-2-thienyl)-5,6-dihydro-1,4,2-oxathiazine-4-oxide (mp 102°C, 11.4g, Found: C 35.82, H 2.56, N 5.89, C₇H₆ClNO₂S₂ requires C 35.67, H 2.55, N 5.94).

Example 4

Synthesis of 1,4,2-oxathiazine, 5,6-dihydro-6-methyl-3-(2-thienyl)- (Compound #52)

Methyl-2-thiophenecarbodithioate (47g, 0.27 mol) in methanol (250 ml) at 0-5°C, was stirred and treated with powdered hydroxylamine hydrochloride (20g) and followed by dropwise addition of triethylamine (50 ml) in methanol (50 ml) over 2 hours, to prepare a reaction mixture. Additional hydroxylamine hydrochloride (5g) and triethylamine (10 ml) was added consecutively to the reaction mixture and after 45 minutes, the reaction mixture turned yellow (from red). 1,2-Dibromopropane (26 ml) was then added to the yellow reaction mixture, followed by addition of triethylamine (75 ml). The resultant new reaction mixture was refluxed for 4 hours and then left overnight at ambient temperature. The methanol was removed from the reaction mixture to leave a residue. Water was added to the residue which was then extracted into ethyl acetate, washed with dilute hydrochloric acid (2N, 100 ml), water, and dried (MgSO₄). The ethyl acetate was then removed to leave a brown oil which was crystallized with cyclohexane to produce two crops of 5,6-dihydro-6-methyl-3-(2-thienyl)-1,4,2-oxadiazine (11.7g and 3.7g, mp 70-72°C) Found: C 48.90, H 4.66, N 7.17, C₈H₉NOS₂ requires C 48.24, H 4.52, N 7.07

Example 5

Synthesis of 5,6-dihydro-6-methyl-3-(2-thienyl)-1,4,2-oxathiazine-4,4-dioxide (Compound #51)

The 5,6-dihydro-6-methyl-3-(2-thienyl)-1,4,2-oxathiazine produced in Example 4 above (2.8g, 0.013 mol), was oxidized with m-chloroperoxybenzoic acid (9.8g) as described in Example 1. Excess peroxide was destroyed with aqueous sodium bisulphite. Extraction produced 5,6-dihydro-6-methyl-3-(2-thienyl)-1,4,2-oxathiazine-4,4-dioxide (from ethanol) (2.1g, mp 147-148°C). Found C 42.06, H 3.99, N 6.08, C₈H₉NO₃S₂ requires C 41.56, H 3.90, N 6.06.

Example 6

Synthesis of 5,6-dihydro-6-methyl-3-(2-thienyl)-1,4,2-oxathiazine-4-oxide Compound #50)

The 5,6-dihydro-6-methyl-3-(2-thienyl)-1,4,2-oxadiazine produced in Example 4 above (2.8g, 0.013 mol), was oxidized with m-chloroperoxybenzoic acid (3.7g) as described in Example 1. The resultant product was recrystallized from ethanol to produce 5,6-dihydro-6-methyl-3-(2-thienyl)-1,4,2-oxathiazine-4-oxide (1.3g, mp 114-115°C). Found C 44.85, H 4.31, N 6.54, C₈H₉NO₂S₂ requires C 44.65, H 4.19, N 6.51.

Example 7

Synthesis of 5,6-dihydro-3-(2-benzothiazolyl)-1,4,2-oxathiazine (Compound #84)

Methyl 2-benzothiazolecarbodithioate (37g, 0.16 mol) was converted to 1,4,2-oxathiazine using hydroxylamine

hydrochloride (13.2g) and triethylamine (33 ml) as described in Example 4. The ethyl acetate extract of the product was washed successively with diluted hydrochloric acid (2N), water, 5% sodium hydroxide and water. Evaporation of the solvent left a solid residue which was recrystallized from ethanol/ethyl acetate to 5,6-dihydro-3-(2-benzothiazolyl)-1,4,2-oxathiazine (18.0g, mp 150-151°C) Found C 50.68, H 3.27, N 11.78, $C_{10}H_8N_2OS_2$ requires C 50.85, H 3.39, N 11.80.

Example 8

Synthesis of 5,6-dihydro-3-(2-benzothiazolyl)-1,4,2-oxathiazine-4,4-dioxide (Compound #83)

The 5,6-dihydro-3-(2-benzothiazolyl)-1,4,2-oxathiazine produced in Example 7 (4.2g, 0.018 mol) was oxidized with m-chloroperoxybenzoic acid as described in Example 5, to produce 5,6-dihydro-3-(2-benzothiazolyl)-1,4,2-oxathiazine 4,4-dioxide (3.7g, mp 226-227°C). Found C 44.59, H 3.01, N 10.31, $C_{10}H_8N_2O_3S_2$ requires C 44.78, H 2.99, N 10.45.

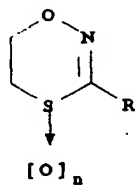
Example 9

Synthesis of 5,6-dihydro-3-(2-benzothiazolyl)-1,4,2-oxathiazine-4-oxide (Compound #85)

The 5,6-dihydro-3-(2-benzothiazolyl)-1,4,2-oxathiazine produced in Example 7 was oxidized as described in Example 6 to produce 5,6-dihydro-3-(2-benzothiazolyl)-1,4,2-oxathiazine-4-oxide (2.3g, mp 192-195°C). Found C 47.96, H 3.26, N 11.22, $C_{10}H_8N_2O_2S_2$ requires C 47.62, H 3.17, N 11.11.

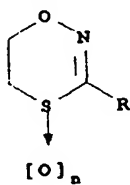
Tables 1-4 list representative compounds numbered 1-107.

TABLE I



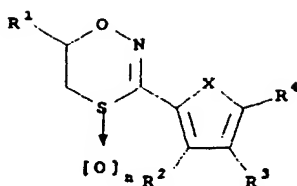
Compound #	n	R
1	1	4-chlorophenyl
2	2	2,4-dichlorophenyl
3	1	3-nitrophenyl
4	1	3,4-dichlorophenyl
5	2	2-methylphenyl
6	1	3-fluorophenyl
7	1	2-furanyl
8	1	2-thienyl
9	1	3-methoxyphenyl
10	1	4-methylphenyl
11	2	4-methylphenyl
12	2	2-furanyl
13	1	3-trifluoromethylphenyl
14	1	4-ethanonephenyl
15	1	2,6-dichlorophenyl

TABLE I (CONT)



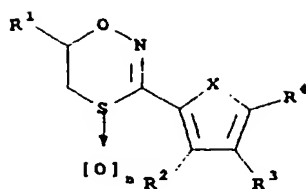
Compound #	n	R
16	2	2,6-dichlorophenyl
17	2	phenyl
18	2	4-chlorophenyl
19	2	3,5-dichlorophenyl
20	1	4-butoxyphenyl
21	1	3,5-dichlorophenyl
22	1	4-benzoic acid, ethyl ester
23	2	3-chlorophenyl
24	2	4-trifluoromethylphenyl
25	1	4-trifluoromethylphenyl
26	1	3-benzoic acid, methyl ester
27	2	3-bromophenyl
28	1	4-ethoxyphenyl

TABLE 2



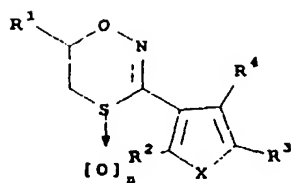
CMPD #	R¹	R²	R³	R⁴	X	n	M.P. (°C)
29	H	H	H	CO₂CH₃	O	0	85-89
30	H	H	H	CO₂CH₃	O	2	126-129
31	H	H	H	CO₂CH₃	O	1	118-119
32	H	CH₃	H	H	S	0	oil
33	H	CH₃	H	H	S	1	73-75
34	H	H	H	H	S	2	99-101
35	H	H	H	Br	S	0	82-83
36	H	H	H	Br	S	1	113-114
37	H	CH₃	H	H	S	2	60-62
38	H	H	H	Br	S	2	118-119
39	H	H	CO₂CH₃	CH₃	O	0	87-88
40	H	H	Br	H	S	0	74-75
41	H	H	Br	H	S	1	169-173
42	H	H	Br	H	S	2	126-127
43	H	H	CO₂CH₃	CH₃	O	2	156-157
44	H	H	CO₂CH₃	CH₃	O	1	147-148
45	H	H	CH₃	CO₂CH₃	S	1	150-152
46	H	H	CH₃	CO₂CH₃	S	2	125-126
47	H	H	H	CH₃	S	0	62-63
48	H	H	H	CH₃	S	1	109-111
49	H	H	H	CH₃	S	2	101-102
50	CH₃	H	H	H	S	1	114-115
51	CH₃	H	H	H	S	2	147-148
52	CH₃	H	H	H	S	0	70-72
53	H	H	H	CO₂CH₂CH₃	S	0	68-69

TABLE 2 (CONT)



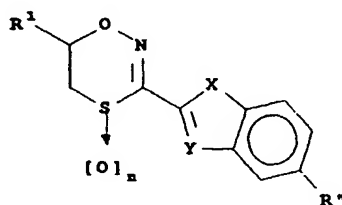
CMPD #	R ¹	R ²	R ³	R ⁴	X	n	M.P. (°C)
54	H	H	H	CO ₂ CH ₂ CH ₃	S	1	109-110
55	H	H	H	CO ₂ CH ₂ CH ₃	S	2	123-124
56	H	H	H	CN	S	0	136-137
57	H	H	H	CN	S	1	160-162
58	H	H	H	CN	S	2	153-155
59	H	H	H	Cl	S	0	74-77
60	H	H	H	Cl	S	1	102
61	H	H	H	Cl	S	2	113-114
62	H	H	H	CHO	S	0	48-49
63	H	H	H	NO ₂	S	0	162-163
64	H	H	H	NO ₂	S	1	186-188
65	H	H	H	NO ₂	S	2	160-161
66	H	H	H	CH=NOCH ₃	S	2	168-170
67	H	H	H	C ₆ H ₅	S	0	100-103
68	H	H	H	C ₆ H ₅	S	1	144-147
69	H	H	H	C ₆ H ₅	S	2	95-98
70	H	H	NO ₂	C ₆ H ₅	S	0	140-145
71	H	H	CH ₃	Br	S	0	oil
72	H	H	CH ₃	Br	S	1	100-104
73	H	H	Br	CH ₃	S	0	64-67
74	H	H	COOH	CH ₃	O	0	188-189
75	H	H	CONHC ₆ H ₅	CH ₃	O	0	176-178
76	H	H	CONHC ₆ H ₅	CH ₃	O	1	182-183
77	H	H	CONHC ₆ H ₅	CH ₃	O	2	193-194

TABLE 2A



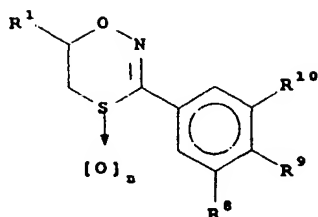
CMPD #	R¹	R²	R³	R⁴	X	n	M.P. (°C)
78	H	H	H	H	S	2	102-104
79	H	H	H	H	S	1	106-107

TABLE 3



CMPD #	R¹	R²	X	Y	n	M.P. (°C)
80	H	H	O	N	2	255
81	H	H	O	N	1	190-191
82	H	H	O	N	0	143-144
83	H	H	S	N	2	226-227
84	H	H	S	N	0	150-151
85	H	H	S	N	1	192-195
86	H	H	S	CH	0	132-134
87	H	H	S	CH	1	140-142
88	H	H	S	CH	2	150-154
89	H	CH₃	O	N	1	209-210
90	H	CH₃	O	N	2	215-216
91	H	H	S	C-OCH(CH₃)₂	1	oil

TABLE 4



CMPD #	R ¹	R ⁸	R ⁹	R ¹⁰	n	M.P.(°C)
92	H	H	F	H	2	136-138
93	H	H	F	H	1	132-133
94	H	F	F	H	2	106-108
95	H	F	F	H	1	128-130
96	H	F	F	H	0	63-65
97	H	CF ₃	H	CF ₃	1	110-113
98	H	CF ₃	H	CF ₃	0	44-48
99	H	CF ₃	H	CF ₃	2	76-78
100	H	F	H	F	0	103-104
101	H	F	H	F	2	108-110
102	H	F	H	F	1	138-139
103	H	CO ₂ CH(CH ₃) ₂	Cl	H	0	oil
104	H	CO ₂ CH(CH ₃) ₂	Cl	H	1	127-129
105	H	CO ₂ CH(CH ₃) ₂	Cl	H	2	82-83
106	H	H	CH-NOCH ₃	H	1	85-87
107	H	H	CH-NOCH ₃	H	2	104-106

Examples of Biological Activity

Example 10

Wood Preservative Efficacy Against Bacteria and Yeasts

Compositions were prepared by dissolving the compounds shown in Table 1 in 50% ethanol and further diluting with sterile distilled water. These dilutions were pipetted into Petri dishes and mixed with warm tryptose agar to reach an active ingredient concentration of 10 and 100 ppm. After cooling, the medium was inoculated with the bacteria listed below. After sufficient growth of the untreated cultures, the compounds were evaluated using the following rating system:

- 0 = growth equal to control
1 = inhibition of growth by the compound

EP 0 715 625 B1

2 = no growth under the influence of the compound. The scores measured for wood preservation efficacy of the compounds of this invention are listed in Table 5. In this Table, the higher numbers are the most preferred species.

Causal agents: Bacteria/Yeasts

5

Debaryomyces hansenii (yeast)
Pseudomonas alcaligenes (gram neg)
Bacillus cereus mycoides (gram pos)
Pseudomonas aeruginosa (gram neg)

10

Flavobacterium sp. (gram neg)
Streptomyces albus (gram pos)
Enterobacter aerogenes (gram neg)
Escherichia coli (gram pos)

15

20

25

30

35

40

45

50

55

TABLE 5

DETAILED SCORES OF THE BACTERICIDAL ACTIVITY OF THE TEST COMPOUNDS																
	Palcal- genes	B.cereus mycoides		Paeruginosa		D.hansenii		Flavobacter		S. albus		E.aerogenes		E. Coli		
Conc. (ppm)	100	100	10	100	100	100	10	100	10	100	10	100	10	100	10	
Aq. Dist.	0	0	0	0	0	0	0	0	-	0	-	0	-	0	-	
EtOH	0	0	0	0	0	0	0	0	-	0	-	0	-	0	-	
CMPD #																
1	1	2	2	0	0	2	2	2	2	2	2	0	2	2	-	
2	0	2	0	0	0	2	2	2	-	0	-	0	-	0	-	
3	2	2	2	1	1	2	1	2	-	2	-	1	-	2	-	
4	1	2	2	0	0	2	2	2	-	2	-	0	-	2	-	
5	0	2	0	0	0	2	0	2	-	2	-	0	-	1	-	
6	1	2	0	0	0	2	2	2	-	2	-	0	-	2	-	
7	1	2	0	0	0	2	0	2	-	2	-	0	-	0	-	
8	2	2	0	0	1	2	2	2	-	2	-	2	-	2	-	
9	0	0	0	0	0	2	0	2	-	0	-	0	-	0	-	
10	1	2	0	1	1	2	2	2	-	2	-	0	-	2	-	
11	1	1	0	1	1	2	0	2	-	1	-	0	-	0	-	
12	0	0	0	0	0	2	0	2	-	0	-	0	-	0	-	
13	0	2	2	0	0	2	2	2	-	2	-	0	-	2	-	
14	1	2	2	1	1	2	0	2	-	2	-	0	-	2	-	
15	0	1	0	0	0	1	0	0	-	0	-	0	-	0	-	
16	0	2	0	0	0	2	0	0	-	0	-	0	-	0	-	
17	0	0	0	0	0	-	-	0	0	0	0	0	0	0	0	
18	1	2	0	0	0	-	-	2	0	2	0	0	0	0	0	
19	0	2	0	0	0	-	-	2	0	2	0	0	0	0	0	
20	0	0	0	0	0	-	-	0	0	2	0	0	0	0	0	
21	2	2	2	0	0	-	-	2	2	2	2	0	0	0	0	
22	1	2	2	2	0	-	-	2	1	2	1	0	0	0	0	
23	0	0	0	0	0	-	-	0	0	2	0	0	0	0	0	
24	0	2	2	2	0	-	-	2	0	2	1	0	0	0	0	
25	1	2	2	2	0	-	-	2	1	2	2	2	0	0	0	
26	0	2	2	2	0	-	-	2	0	2	2	0	0	0	0	

TABLE 5 (continued)

DETAILED SCORES OF THE BACTERICIDAL ACTIVITY OF THE TEST COMPOUNDS															
	P.alcal- genes	B.cereus mycoides		P.aeruginosa		D.hansenii		Flavobacter		S. albus		E.aerogenes		E. Coli	
Conc. (ppm)	100	100	10	100	100	100	10	100	10	100	10	100	10	100	10
27	1	2	2	0	-	-	-	2	2	2	2	0	0	2	1
28	0	2	1	0	-	-	-	2	0	2	1	0	0	0	0
Notes for Table 5 Ratings:															
0 = growth equal to control															
1 = inhibition of growth by the compound															
2 = no growth under influence of the compound															

Example 11Wood Preservative Efficacy Against Fungi

5 The compounds shown in Table 1 were dissolved in 50% ethanol and then diluted with sterile water to give the required concentrations of 1 and 10 ppm in the test agar plates. Malt extract sugar (3%) was added aseptically and uniform distribution was obtained by shaking. Each plate was inoculated with a spore suspension or with a small piece of agar (1 mm) from the margin of an actively growing colony of the test fungus. The fungi employed are listed below. After incubation at 22°C and 70% relative humidity during a period long enough to allow significant growth of untreated controls, the diameters of the fungus colonies were measured and scored using the following rating system:

- 10
- 0 = free of fungal growth
 1 = 25% of fungal growth compared to untreated
 2 = 50% of fungal growth compared to untreated
 15 3 = 75% of fungal growth compared to untreated
 4 = Growth equal to that of untreated

The scores measured for wood preservation efficacy of the compounds of this invention are listed in Tables 6a and 6b. In these Tables, the lower numbers are the most preferred species.

20 Causal agents: Fungi

- Coriolus versicolor
 Coniophora puteana (syn. C. cerebella)
 Chaetomium globosum
 25 Aureobasidium pullulans
 Penicillium islandicum
 Cladosporium resinae (syn Hormonocanis resinae, Amorphantheca resinae)
 Aspergillus niger
 Aspergillus flavus
 30 Trichoderma viride
 Mucor sp.

35

40

45

50

55

TABLE 6A

DETAILED SCORES OF FUNGICIDAL ACTIVITY OF TEST COMPOUNDS										
(Test Dosage: 10 ppm)										
CMPD#	C. VERSICOLOR	C. PUTEANA	C. GLOBOSUM	MUCOR SP	A. PULLULANS	P. ISLANDICUM	CL RESINAE	A. NIGER	A. FLAVUS	T. VIRIDE
CNTRL	4	4	4	4	4	4	4	4	4	4
1	0	2	0	-	3	0	2	0	0	2
2	2	4	4	-	4	4	3	4	4	2
3	0	2	3	-	3	3	4	3	2	3
4	0	0	0	-	2	0	0	0	0	1
5	3	4	4	-	4	4	4	4	4	4
6	1	0	4	-	3	3	4	3	2	4
7	3	4	4	-	4	4	4	4	4	4
8	0	2	2	-	2	0	2	1	1	2
9	4	4	4	4	4	4	4	4	4	4
10	1	3	4	0	4	3	4	4	2	3
11	0	0	4	0	4	0	4	0	1	2
12	4	4	4	4	4	4	4	4	4	4
13	0	1	0	0	2	2	3	1	2	3
14	2	3	4	1	4	4	0	3	2	3
15	0	4	4	4	4	0	4	3	3	4
16	0	4	4	4	0	0	4	2	4	0

NOTES:

Rating Scale for Table 6A

0 = free of fungal growth

1 = 25% of growth compared to untreated control

2 = 50% of growth compared to untreated control

3 = 75% of growth compared to untreated control

4 = growth equal to that of untreated control

TABLE 6B

DETAILED SCORES OF THE FUNGICIDAL ACTIVITY OF THE TEST COMPOUNDS													
	G. VERSICLOR		G. PUTEANA		C. GLO-BOSUM	MUCOR SP		A. PULLULANS	P. ISLANDICUM	CL. RESINAE	A. NIGER	A. FLAVUS	T. VIRIDE
CONC (ppm)	10	1	10	1	10	100	10	10	10	10	10	10	10
Aq. Dist.	4	4	4	4	4	4	4	4	4	4	4	4	4
EtOH	4	4	4	4	4	4	4	4	4	4	4	4	4
CMPD #													
17	4		4		4	4		4				4	
18	0	1	0		0	0		0	0	1	0	0	2
19	0	2	3		0	2		3	0	0	0	0	2
20	4		4		4	4		4	4	4	4	4	4
21	0	3	0		2	0	1	2	0	0	0	0	4
22	2		0	3	4	0		4	2	4	3	2	3
23	4		4		4	4		4	4	4	4	4	4
24	0		3		4	4		4	0	0	0	0	2
25	0	3	0	2	3	0	3	3	1	0	0	0	2
26	4		4		4	2		4	4	4	4	4	3
27	0		0	3	4	0		4	4	0	3	3	2
28	3		0		4	1		4	4	4	4	3	3

NOTES:

Rating Scale for Table 6B

0 = free of fungal growth

1 = 25% of growth compared to untreated control

2 = 50% of growth compared to untreated control

3 = 75% of growth compared to untreated control

4 = growth equal to that of untreated control

Example 12Control of Molds and Blue Stain Fungi in Stick Test

The compounds shown in Table 1 were dissolved in 50% ethanol and a dilution series was made using the same solvent. In 25 ml of each dilution, one oven-dried beech stick (73 x 18 x 2 mm) was drenched until saturated.

Test dosages were 50, 100, 250, 500, and 1000 ppm for blue stain fungi which were *Aureobasidium pullulans* and *Sclerophoma pithyophila*. Test dosages for the molds used (*Trichoderma viride*, *Aspergillus niger*) were 250, 500, 1000, 2500, and 5000 ppm.

After three hours the test solution was poured off and each stick was allowed to dry in a sterile laminar air flow. In each Petri dish one stick was placed on malt agar previously seeded with inoculum. Two drops of fungal or spore suspension were pipetted on the upper surface of the stick. The Petri dishes were then incubated at 22°C and 90% relative humidity. The treated sticks were evaluated after sufficient growth of the fungus on the untreated control sticks. The following score system was used to rate the effectiveness of the compounds:

- 0 = stick free of fungal growth
- 1 = traces of fungal growth on stick
- 2 = slight fungal growth (5 to 25% of the surface covered)
- 3 = moderate fungal growth (25 to 50% of the surface covered)
- 4 = vigorous fungal growth (greater than 50% of the surface covered).

For purposes of comparison of these compounds, these values were converted to threshold ranges. The threshold value in this system is defined as the minimum concentration of a particular compound which produces a score less than or equal to 1. These values are presented in Table 7.

TABLE 7

THRESHOLD VALUES (PPM) OF TEST COMPOUNDS IN STICK TEST				
FUNGI				
COMPOUND #	AUREOBASIDIUM PULLULANS	SCLEROPHOMA PYTHIOPHILA	ASPERGILLUS NIGER	TRICHODERMA VIRIDE
1	>1000	100-250	1000-2500	2500-5000
4	500-1000	50-100	250-500	500-1000
8	250-500	50-100	250-500	500-1000
11	1000	<50	500-1000	2500-5000
13	500-1000	250-500	500-1000	1000-2500
16	>1000	100-250	>5000	>5000
18	500-1000	100-250	250-500	<250
19	250-500	250-500	250-500	<250
21	250-500	50-100	<250	<250
24	500-1000	250-500	250-500	500-1000
25	250-500	50-100	<250	<250
27	>1000	500-1000	500-1000	<250

Example 13Activity Against Wood-Rotting Fungi such as *Coriolus versicolor* and *Coniophora puteana*

Sapwood blocks (50 x 20 x 6 mm) of Scots pine (*Pinus sylvestris*) and beech (*Fagus sylvatica*) were oven-dried at 104°C. The blocks were cooled, weighed, and impregnated with the test compound, by a vacuum treatment. Each concentration of the test compounds was applied to 7 replicates. By reweighing after each treatment, the uptake of active ingredient was calculated. Badly treated wood was discarded. For fixation of the active compound, the treated

EP 0 715 625 B1

blocks were kept in a closed container for two weeks. The container was opened and the wood was dried for two more weeks. The test blocks were sterilized by gamma-irradiation (1.2 Mrad) . Each treated block was placed on a mesh in an inoculated Petri dishes of malt agar, with an untreated (control) block.

All the blocks were exposed to fungal attack for eight weeks at 22°C and 70% relative humidity. At the end of the incubation period, the blocks were freed from adhering mycelium, oven dried at 104°C, allowed to cool, and weighed. The percentage weight loss of each block was calculated. Invalid results, due to waterlogging or insufficient moisture content, were not taken into account.

The average weight loss of the treated blocks compared to the control blocks appears in Table 8.

TABLE 8

AVERAGE WEIGHT LOSS OF BLOCKS TREATED WITH TEST COMPOUNDS						
CMPD #	CORIOLUS			CONIOPHORA		
	UPTAKE g.a.i./m3	% WEIGHT LOSS		UPTAKE g.a.i./m3	% WEIGHT LOSS	
		TREATED	CONTROL		TREATED	CONTROL
4	477	35	32	568	0.3	17
	1205	35	41	1356	0.3	21
6	482	25	33	555	0.0	29
	1163	19	41	1373	-0.1	20
8	494	24	34	536	0.9	25
	1184	3.5	26	1346	0.7	31
11	485	5.4	29	530	ND	ND
	1162	8.3	30	1346	1.8	28
13	492	27	31	530	-0.2	34
	1202	9.0	31	1271	0.1	32
18	488	32	31	579	0.0	41
	1173	39	40	1534	-0.3	35
19	472	35	29	573	0.9	42
	1222	87	35	1456	-0.3	37
21	496	38	35	582	-0.1	42
	1203	22	33	1456	-0.5	35
24	450	39	37	545	17.3	30
	1136	35	39	1374	0.9	29
25	482	37	38	533	-0.7	30
	1175	21	44	1358	-0.8	33
27	479	32	31	526	0.7	36
	1203	36	37	1347	-0.5	34
NOTES FOR TABLE 8: ND = NO DATA						

Example 14

In Vitro Activity Against Molds and Blue-Stain Fungi

Representative compounds were dissolved (2000 ppm) in a 2:3 solution of acetone:ethanol. The effect of the representative compounds on the growth of certain molds and blue-stain fungi were determined using a poison plate assay according to the following procedure: The solutions of the representative compounds prepared above were further diluted with sterile water to desired concentrations and poured into Petri dishes. Malt extract agar medium was then added aseptically to the Petri dishes and to Petri dishes containing no compound (controls). The Petri dishes were then shaken to provide a uniform distribution of the agar medium. Each Petri dish containing compound and each control Petri dish, was then inoculated with a fungus and incubated for a period of time sufficient to permit complete growth of the fungus in the respective control Petri dish. The Petri dishes containing compound were then examined to determine the amount of inhibition of fungi for each concentration of compound tested. The lowest concentration of compound which resulted in complete inhibition of a particular fungus was determined and recorded in Tables 9A and 9B below as the minimum inhibitory concentration (MIC) values.

TABLE 9A

MIC (ppm) of Compounds against Fungi									
Compound #	8	34	57	58	60	61	83	85	87
A. amstelodami	10	5	10	5	5	5	>25	5	5
A. niger	25	5	10	5	5	<1	>25	5	2.5
A. versicolor	10	5	10	5	2.5	2.5	25	2.5	2.5
A. pullulans	>25	25	>25	25	25	10	>25	25	10
C. cladosporioides	>25	25	25	10	25	10	>25	25	25
C. pilifera	5	2.5	10	5	5	2.5	10	2.5	2.5
F. solani	25	25	25	10	10	5	>25	25	10
G. candidum	>25	25	25	25	25	10	>25	10	25
P. purpurogenum	>25	10	10	10	25	5	>25	10	2.5
P. variotii	>25	25	25	25	10	5	>25	25	10
P. violacea	25	25	25	25	10	25	>25	10	10
S. atra	10	5	10	5	5	2.5	5	2.5	2.5
S. entoxylina	10	5	10	5	5	10	10	5	5
T. viride	>25	>25	>25	25	25	10	>25	25	10
U. atrum	25	25	25	10	10	10	>25	10	10

TABLE 9B

MIC (ppm) of Compounds against Fungi				
Compound #	A	4	19	21
A. amstelodami	25	10	25	10
A. niger	5	2.5	2.5	5
A. versicolor	10	5	25	2.5
A. pullulans	10	10	25	25
C. cladosporioides	25	10	25	25
C. pilifera	10	5	10	2.5
F. solani	>25	10	>25	10

TABLE 9B (continued)

MIC (ppm) of Compounds against Fungi				
Compound #	A	4	19	21
G. candidum	>25	25	>25	25
P. purpurogenum	10	10	25	10
P. variotii	25	10	25	10
P. violacea	>25	25	>25	10
S. atra	10	2.5	25	2.5
S. entoxylina	25	10	25	10
T. viride	25	25	25	25
U. atrium	>25	25	>25	10
A = 3,4-dichlorophenyl-1,4,2-oxathiazine (Compound 4 of Table 1 except that n = 0) (Compound A can be prepared utilizing the procedures described in U. S Patent No. 4,569,690.)				

Example 15Activity against Blue-Stain Fungi and Molds on a Stick Test on Vermiculite

Beech sticks (73x18x2 mm) *Fagus sylvatica* were painted, allowed to dry, and sterilized by γ -radiation (1.2 mRad). Sticks were treated by coating each stick with a film containing 0.15% or 0.3% of the tested compound in a water-based placebo paint.

The coated sticks prepared above were then dipped in a spore suspension of pure culture of each fungus. Seven sticks each were placed in autoclaved Petri dishes (200 mm in diameter, 30 mm in height) containing 300 ml of vermiculite and 120 ml of water, and incubated for 12 weeks. The surfaces of the sticks were then examined for the growth of fungus and were evaluated according to the following scoring system:

- 0: No growth
- 1: Trace of growth of up to 1% coverage of the test inoculated area
- 2: Growth covering between 1 and 10% of the inoculated test area
- 3: Growth covering between 10 and 30% of the inoculated test area
- 4: Growth covering between 30 and 70% of the inoculated test area
- 5: Growth covering more than 70% of the inoculated test area.

The scores of compounds tested are presented in Table 10.

TABLE 10

Surface Scores of Wooden Sticks Treated with Paint Formulation															
Organisms	Compounds/% a.i.														
	8		34		36		37		38		41		42		Control
	0.15	0.3	0.15	0.3	0.15	0.3	0.15	0.3	0.15	0.3	0.15	0.3	0.15	0.3	
A. versicolor	0	0	0	0	0	0	2	1	1	0	0	0	2	1	5
A. pullulans	0	0	0	0	0	0	3	2	2	0	0	0	2	1	5
C. cladosporioides	0	0	0	0	0	0	3	0	2	0	0	0	2	1	5
P. purpurogenum	0	0	4	1	1	1	3	1	3	3	2	1	4	2	5
P. violacea	4	0	4	1	3	1	5	4	4	4	4	3	4	3	5
R. rubra (y)	1	1	3	0	0	0	4	3	3	0	3	0	3	1	5
S. chartarum	0	0	1	0	0	0	1	0	5	2	4	0	3	2	5
U. atrum	1	1	3	1	3	1	4	3	4	3	3	1	5	3	5
y = yeast															
0 = No growth															
1 = Trace of growth of up to 1% coverage of the test inoculated area.															
2 = Growth more than 1% and up to 10% coverage of test inoculated area.															
3 = Growth more than 10% and up to 30% coverage of test inoculated area.															
4 = Growth more than 30% and up to 70% coverage of test inoculated area.															
5 = Growth more than 70% coverage of test inoculated area.															

Example 16Activity against Blue-Stain Fungi and Molds in a Stick Test

Representative compounds of this invention were dissolved in 50% ethanol. Each compound was then diluted serially using 50% ethanol. Four (4) oven-dried beech sticks (73 x 18 x 2 mm) were drenched until saturated in 25ml of each dilution of each compound, to prepare the treated sticks. After three (3) hours, the solutions containing the test compounds were poured off and the treated sticks were allowed to dry in a sterile laminar air flow. Each treated stick was then placed in a Petri dish which had been previously seeded with inoculum. Two drops of a test fungal or spore suspension were pipetted onto the upper surface of each treated stick. The Petri dishes containing the treated sticks were incubated at 22°C and 90% relative humidity. The treated sticks were evaluated after there was sufficient growth of fungus on control sticks (i.e., untreated sticks) incubated in the same manner. The following score system was used:

- 0: Stick free of fungal/mold growth
- 1: Traces of fungal growth on the stick
- 2: Slight growth (5 to 25% of the surface covered with fungal growth)
- 3: Moderate growth (25 to 50% covered with fungal growth)
- 4: Vigorous to maximum fungal growth (more than 50% growth)

The threshold (minimum) concentration of each compound tested necessary to obtain a score of 1-2 or 0, for each fungus tested is presented in Table 11 below.

TABLE 11

Threshold Concentrations (ppm) against Blue-stain Fungi and Molds in a Stick Test								
CMPD #	Fungi/Mold							
	Aureobasidium		Sclerophoma		A. niger		Trichoderma	
	score 1-2	score 0	score 1-2	score 0	score 1-2	score 0	score 1-2	score 0
8	250-500	>1000	50-100	100	250-500	1000	500-1000	1000
34	250-500	>1000	<50	100	<250	500	500-1000	2500
50	100-500	>1000	50-100	100	250-500	1000	1000-2500	5000
51	250-500	>1000	50-100	100	250-500	500	500-1000	1000
54	250-500	500	<50	100	<250	500	500-1000	5000
57	250-500	>1000	<50	100	<250	500	500-1000	1000
58	500-1000	>1000	<50	100	<250	500	1000-2500	5000
60	100-250	1000	<50	100	<250	500	500-1000	2500
61	250-500	>1000	<50	100	<250	<250	1000-2500	2500
81	250-500	>1000	<50	250	250-500	500	500-1000	2500
85	250-500	1000	<50	100	<250	1000	1000-2500	2500
87	100-250	1000	50-100	100	250-500	1000	1000-2500	5000
89	100-250	>1000	<50	250	250-500	500	1000-2500	2500
0: Stick free of fungal growth								
1: Traces of fungal growth on the stick								
2: Slight growth (5 to 25% of the surface covered with fungal growth)								

Example 17Activity against Blue-Stain Fungi and Molds in a Mold Cabinet Test

Using the methods described in BS3900: Part G6: 1989, British Standard Methods of test for paints, "Assessment of resistance to fungal growth", representative compounds of this invention were tested for activity against blue-stain fungus and molds in a mold cabinet test.

In brief, sticks of Scots pine (*Pinus sylvestris*) measuring 75 x 100 x 10 mm, were painted, allowed to dry, and sterilized by γ -radiation (1.2 mRad).

Solutions of the tested compounds (0.15% and 0.3%) in water-based placebo paint were prepared. The sticks were then with each solution. The inoculation consisted of dipping the sticks in a mixed spore suspension, then placing them in a mold chamber and incubating them for 12 weeks. The surfaces were evaluated according the following score system:

- 0: No growth
- 1: Trace of growth of up to 1% coverage of the inoculated test area
- 2: Growth covering between 1 and 10% of the inoculated test area
- 3: Growth covering between 10 and 30% of the inoculated test area
- 4: Growth covering between 30 and 70% of the inoculated test area
- 5: Growth covering more than 70% of the inoculated test area.

The scores of compounds tested are presented in Table 12.

TABLE 12

Surface Scores in a Paint Formulation in a Mold Cabinet Test			
Compound #	Concentration (%)	Surface Score	
		6 weeks	12 weeks
8	0.15	0	2.0
	0.3	0	1.5
34	0.15	0.5	1.5
	0.3	0	1.0
36	0.15	2.5	4.5
	0.3	2.5	4.0
37	0.15	4.0	5.0
	0.3	0	0
38	0.15	2.5	4.5
	0.3	2.5	4.0
41	0.15	0	2.0
	0.3	0.5	3.0
42	0.15	1.5	3.5
	0.3	0.5	3.0
Placebo	-	5.0	5.0
0 = No growth 1 = Trace of growth of up to 1% coverage of the test inoculated area. 2 = Growth more than 1% and up to 10% coverage of test inoculated area. 3 = Growth more than 10% and up to 30% coverage of test inoculated area. 4 = Growth more than 30% and up to 70% coverage of test inoculated area. 5 = Growth more than 70% coverage of test inoculated area.			

Example 18

Control of Molds and Sapstain Fungi in Mini-Board Test

Representative compounds of this invention to be tested, were suspended in an aqueous solution containing 7.5% GENAPOL X 080™ (Hoechst-Celanese Corporation), and 20% propylene glycol monomethyl ether, to prepare the test solutions. The concentration of the test compound in the test solution was 5000 ppm.

Deep frozen boards (300 x 50 x 10 mm) of freshly felled sapwood of *Pinus sylvestrus* (mini-boards) were thawed at room temperature. One half of each mini-board was immersed in a test solution for 20 seconds. The mini-boards were then sprayed with mixed spore suspension containing the following fungi:

- 5 *Aureobasidium pullulans*,
 Aspergillus amstelodami,
 Ceratocystis pilifera,
 Cladosporium sp.,
 Penicillium sp.,
 10 *Sclerophomas entoxylina*, and
 Trichoderma viride,

and stored in incubation boxes at 25°C and at 100% relative humidity, for three weeks. For each compound tested, each concentration of test solution was applied to five different mini-boards.

- 15 The efficacy of the test compounds was determined by comparing the fungal growth on both the treated and untreated parts of the mini-boards.

The degree of infection was scored according to the following scale:

- 0 = Free of fungal growth
 20 1 = Traces of fungal growth
 2 = Little fungal growth
 3 = Moderate fungal growth
 4 = Vigorous to maximum growth (all surfaces covered with fungal growth)

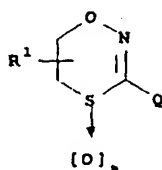
- 25 The results of the mini-board evaluation are presented in Table 13 below.

TABLE 13

Surface Scores of Treated Mini-Boards				
CMPD #	3 Week Incubation		6 Week Incubation	
	1500 ppm	2500 ppm	1500 ppm	2500 ppm
8	0	0	0.8	0.4
34	0	0	2.4	2.4
35 36	0.2	0	2.6	1.4
37	0	0	0.8	0.4
38	0.6	0.4	2.0	2.8
41	0.6	0.2	2.4	1.6
42	0	0	2.0	2.6
40 48	0	0	1.4	0.8
49	0	0	1.8	1.2
78	0.2	0.2	1.2	1.8
79	1.0	0	3.0	1.8
0 = Free of fungal growth 1 = Traces of fungal growth 2 = Little fungal growth 3 = Moderate fungal growth 4 = Vigorous to maximum growth (all surfaces covered with fungal growth)				

Claims

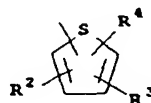
1. A compound of the formula



(I)

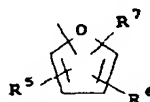
wherein n is 0, 1 or 2; R₁ is hydrogen, C₁-C₄ linear or branched alkyl, or benzyl; and Q is:

(a)



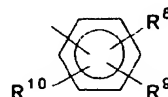
wherein R², R³ and R⁴ are, individually, hydrogen, alkyl, alkoxy, alkylthio, alkoxycarbonyl, halogen, trihalomethyl, cyano, acetyl, formyl, benzoyl, nitro, alkoxyaminomethyl, phenyl or phenylaminocarbonyl, wherein the alkyl or alkoxy moieties are all C₁-C₄, linear or branched, with the proviso that at least one of R², R³ or R⁴ must be other than hydrogen;

(b)



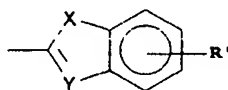
wherein R⁵, R⁶ and R⁷ are, individually, hydrogen, C₁-C₄ alkoxy, C₁-C₄ alkylthio, halogen, trihalomethyl, cyano, acetyl, formyl, benzoyl, nitro, phenyl or phenylaminocarbonyl, with the proviso that at least one of R⁵, R⁶ or R⁷ must be other than hydrogen;

(c)



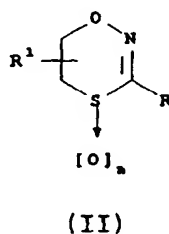
wherein R⁸, R⁹ and R¹⁰ are, individually, hydroxyl, halo, C₁-C₁₂ alkyl, C₅-C₆ cycloalkyl, trihalomethyl, phenyl, C₁-C₅ alkoxy, C₁-C₅ alkylthio, tetrahydropyranyloxy, phenoxy, (C₁-C₄ alkyl)carbonyl, phenylcarbonyl, C₁-C₄ alkylsulfinyl, C₁-C₄ alkylsulfonyl, carboxy or its alkali metal salt, (C₁-C₄ alkoxy)carbonyl, (C₁-C₄ alkyl) aminocarbonyl, phenylaminocarbonyl, tolylaminocarbonyl, morpholinocarbonyl, amino, nitro, cyano, dioxolanyl, or (C₁-C₄ alkoxy)iminomethyl; or

(d)



wherein X is oxygen or sulfur; Y is nitrogen, -CH-, or -C(C₁-C₄ alkoxy)-; and R* is hydrogen or C₁-C₄ alkyl.

2. A compound as recited in claim 1 wherein R¹ is hydrogen or C₁-C₄ alkyl; n is 1 or 2; R², R³ and R⁴ are, individually, hydrogen, C₁-C₄ alkyl, halo, (C₁-C₄ alkoxy)-carbonyl, or cyano, with the proviso that at least one of R², R³ and R⁴ must be other than hydrogen; R⁵, R⁶ and R⁷ are, individually, hydrogen, halo or cyano, with the proviso that at least one of R⁵, R⁶ and R⁷ must be other than hydrogen; R⁸, R⁹ and R¹⁰ are C₁-C₄ alkyl, C₁-C₄ alkoxy, nitro, halo, trihalomethyl, or (C₁-C₄ alkoxy)-carbonyl; X is sulfur; and R* is hydrogen.
3. A compound as recited in claim 2 wherein R¹ is hydrogen; n is 1 or 2; R², R³ and R⁴ are, individually, hydrogen, methyl, ethyl, bromo, chloro, ethyl carboxylate, or cyano, with the proviso that at least one of R², R³ and R⁴ must be other than hydrogen; R⁵, R⁶ and R⁷ are, individually, hydrogen, bromo, chloro or cyano, with the proviso that at least one of R⁵, R⁶ and R⁷ must be other than hydrogen; R⁸, R⁹ and R¹⁰ are methyl, ethyl, nitro, fluoro, chloro, or trifluoromethyl.
4. A method for preserving wood or a composite wood material which comprises treating the wood or the composite wood material with a fungicidally or bactericidally effective amount of a compound of the formula



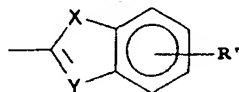
wherein n is 0, 1 or 2; R¹ is hydrogen, C₁-C₄ linear or branched alkyl, or benzyl; and R is:

(a) phenyl; naphthyl; phenyl substituted with 1-3 of the following substituents: hydroxyl, halo, C₁-C₁₂ alkyl, C₅-C₆ cycloalkyl, trihalomethyl, phenyl, C₁-C₅ alkoxy, C₁-C₅ alkylthio, tetrahydropyranyloxy, phenoxy, (C₁-C₄ alkyl) carbonyl, phenylcarbonyl, C₁-C₄ alkylsulfinyl, C₁-C₄ alkylsulfonyl, carboxy or its alkali metal salt, (C₁-C₄ alkoxy) carbonyl, (C₁-C₄ alkyl) aminocarbonyl, phenylaminocarbonyl, tolylaminocarbonyl, morpholinocarbonyl, amino, nitro, cyano, dioxolanyl, or (C₁-C₄ alkoxy)iminomethyl;

pyridinyl; thienyl; furanyl; thienyl or furanyl substituted with 1 to 3 of the following groups:

alkyl, alkoxy, alkylthio, alkoxycarbonyl, halogen, trihalomethyl, cyano, acetyl, formyl, benzoyl, nitro, phenyl or phenylaminocarbonyl, wherein the alkyl or alkoxy moiety is C₁-C₄, linear or branched; or thienyl substituted with 1 to 3 alkoxyaminomethyl, wherein the alkoxy moiety is C₁-C₄, linear or branched; or

(b)

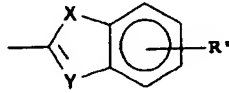


wherein X is oxygen or sulfur; Y is nitrogen, -CH-, or -C(C₁-C₄ alkoxy)-; and R* is hydrogen or C₁-C₄ alkyl.

5. A method as recited in claim 4 wherein R¹ is hydrogen, n is one or two, and R has one or 2 of the following values: phenyl, (C₁-C₆ alkyl)phenyl, halophenyl, dihalophenyl, biphenyl, (C₁-C₅ alkoxy)phenyl, trihalomethylphenyl, nitrophenyl, phenyl substituted with (C₁-C₄ alkoxy)carbonyl, furanyl, furanyl substituted by ethyl carboxylate, cyano, chlorine, or bromine, thienyl, thienyl substituted with ethyl carboxylate, cyano, chlorine, or bromine, or (C₁-C₆ alkyl)nitrophenyl.
6. A method as recited in claim 5 wherein R¹ is hydrogen, n is one or two, and R is represented by: 4-chlorophenyl, 3-nitrophenyl, 3,4-dichlorophenyl, 3-fluorophenyl, 2-thienyl, 4-methylphenyl, 3-trifluoromethylphenyl, 3-ethanone

phenyl, 3,5-dichlorophenyl, 4-trifluoromethylphenyl, or 3-methyl-4-nitrophenyl.

7. A method as recited in claim 4 wherein R¹ is hydrogen, and R is

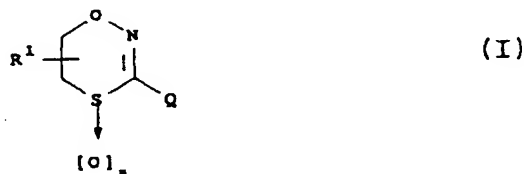


wherein X is sulfur, Y is nitrogen or -CH-, and R* is hydrogen.

8. A method as recited in claim 4 wherein between about 0.05 to 0.4 kg/m² of the compound is applied to the surface area of the wood or the composite wood material.
9. A method as recited in claim 4 wherein about 0.5 to about 6.0 kg/m³ of the compound is applied into the wood or the composite wood material.
10. A composition for preserving wood or a composite wood material which comprises:
- a) an effective amount of a compound as recited in claim 1; and
 - b) a suitable carrier.

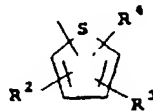
Patentansprüche

1. Verbindung der Formel



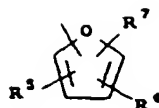
worin $n = 0, 1$ oder 2 ist; R¹ Wasserstoff ein linearer oder verzweigter C₁-C₄-Alkylrest oder ein Benzylrest ist und Q:

(a)



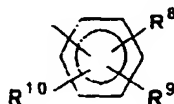
ist, worin R², R³ und R⁴ einzeln Wasserstoff, Alkyl-, Alkoxy-, Alkylthio-, Alkoxycarbonyl-, Halogen-, Trihalogenmethyl-, Cyano-, Acetyl-, Formyl-, Benzoyl-, Nitro-, Alkoxyaminomethyl-, Phenyl- oder Phenylaminocarbonylreste sind, wobei die Alkyl- oder Alkoxyreste alle lineare oder verzweigte C₁-C₄-Reste sind, mit dem Vorbehalt, daß mindestens einer der Reste R², R³ oder R⁴ etwas anderes als Wasserstoff sein muß;

(b)



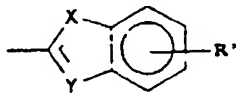
ist, worin R⁵, R⁶ und R⁷ einzeln Wasserstoff, C₁-C₄-Alkoxy-, C₁-C₄-Alkylthio-, Halogen-, Trihalogenmethyl-, Cyano-, Acetyl-, Formyl-, Benzoyl-, Nitro-, Phenyl- oder Phenylaminocarbonylreste sind, mit dem Vorbehalt, daß mindestens einer der Reste R⁵, R⁶ oder R⁷ etwas anderes als Wasserstoff sein muß;

(c)



ist, worin R⁸, R⁹ und R¹⁰ einzeln Hydroxyl-, Halogen-, C₁-C₁₂-Alkyl-, C₅-C₅-Cycloalkyl-, Trihalogenmethyl-, Phenyl-, C₁-C₅-Alkoxy-, C₁-C₅-Alkylthio-, Tetrahydropyranyloxy-, Phenoxy-, (C₁-C₄-Alkyl)carbonyl-, Phenylcarbonyl-, C₁-C₄-Alkylsulfinyl-, C₁-C₄-Alkylsulfonyl-, Carboxyreste oder das Alkalisalz davon, (C₁-C₄-Alk-oxy)carbonyl-, (C₁-C₄-Alkyl)aminocarbonyl-, Phenylaminocarbonyl-, Tolyaminocarbon-, Morpholinocarbonyl-, Amino-, Nitro-, Cyano-, Dioxolanyl- oder (C₁-C₄-Alkoxy)iminomethylreste sind oder

(d)



ist, worin X Sauerstoff oder Schwefel ist; Y Stickstoff, -CH- oder -C(C₁-C₄-Alkoxy)- ist und R* Wasserstoff oder ein C₁-C₄-Alkylrest ist.

2. Verbindung nach Anspruch 1, worin R* Wasserstoff oder ein C₁-C₄-Alkylrest ist; \underline{n} 1 oder 2 ist; R², R³ und R⁴ einzeln Wasserstoff, C₁-C₄-Alkyl-, Halogen-, (C₁-C₄-Alkoxy)carbonyl- oder Cyanoreste sind, mit dem Vorbehalt, daß mindestens einer der Reste R², R³ und R⁴ etwas anderes als Wasserstoff ist; R⁵, R⁶ und R⁷ einzeln Wasserstoff, Halogen- oder Cyanoreste sind, mit dem Vorbehalt, daß mindestens einer der Reste R⁵, R⁶ und R⁷ etwas anderes als Wasserstoff ist; R⁸, R⁹ und R¹⁰ C₁-C₄-Alkyl-, C₁-C₄-Alkoxy-, Nitro-, Halogen-, Trihalogenmethyl- oder (C₁-C₄-Alkoxy)carbonylreste sind; X Schwefel ist und R* Wasserstoff ist.

3. Verbindung nach Anspruch 2, worin R¹ Wasserstoff ist; \underline{n} 1 oder 2 ist; R², R³ und R⁴ einzeln Wasserstoff, Methyl-, Ethyl-, Brom-, Chlor-, Ethylcarboxylat- oder Cyanoreste sind, mit dem Vorbehalt, daß mindestens einer der Reste R², R³ und R⁴ etwas anderes als Wasserstoff sein muß; R⁵, R⁶ und R⁷ einzeln Wasserstoff, Brom-, Chlor- oder Cyanoreste sind, mit dem Vorbehalt, daß mindestens einer der Reste R⁵, R⁶ und R⁷ etwas anderes als Wasserstoff sein muß; R⁸, R⁹ und R¹⁰ Methyl-, Ethyl-, Nitro-, Fluor-, Chlor- oder Trifluormethylreste sind.

4. Verfahren zur Konservierung von Holz oder einem Holzverbundmaterial, umfassend, daß man das Holz oder das Holzverbundmaterial mit einer fungizid oder bakterizid wirksamen Menge einer Verbindung der Formel



behandelt, worin \underline{n} 0, 1 oder 2 ist; R^1 Wasserstoff, ein linearer oder verzweigter C_1 - C_4 -Alkylrest oder Benzylrest ist und R

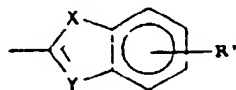
(a) ein Phenylrest, Naphthylrest, mit ein bis drei der folgenden Substituenten:

Hydroxyl, Halogen, C_1 - C_{12} -Alkyl, C_5 - C_6 -Cycloalkyl, Trihalogenmethyl, Phenyl, C_1 - C_5 -Alkoxy, C_1 - C_5 -Alkylthio, Tetrahydropyranyloxy, Phenoxy, (C_1 - C_4 -Alkyl)carbonyl, Phenylcarbonyl, C_1 - C_4 -Alkylsulfinyl, C_1 - C_4 -Alkylsulfonyl, Carboxy oder das Metallsalz, (C_1 - C_4 -Alkoxy)carbonyl, (C_1 - C_4 -Alkyl)aminocarbonyl, Phenylamino-carbonyl, Tolyaminocarbonyl, Morpholinocarbonyl, Amino, Nitro, Cyano. Dioxolanyl oder (C_1 - C_4 -Alkoxy)iminomethyl, substituierter Phenylrest:

Pyridinylrest, Thienylrest, Furanylrest, mit 1 bis 3 der folgenden Gruppen:

Alkyl, Alkoxy, Alkylthio, Alkoxycarbonyl, Halogen, Trihalogenmethyl, Cyano, Acetyl, Formyl, Benzoyl, Nitro, Phenyl oder Phenylaminocarbonyl, worin der Alkyl- oder Alkoxyanteil ein linearer oder verzweigter C_1 - C_4 -Rest ist, substituierter Thienyl- oder Furanylrest, oder ein mit 1 bis 3 Alkoxyaminomethylresten substituierter Thienylrest, worin der Alkoxyanteil ein linearer oder verzweigter C_1 - C_4 -Alkoxyrest ist oder

(b)



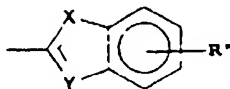
ist, worin X Sauerstoff oder Schwefel ist; Y Stickstoff, -CH- oder -C(C_1 - C_4 -Alkoxy)- ist und R'' Wasserstoff oder ein C_1 - C_4 -Alkylrest ist.

5. Verfahren nach Anspruch 4, worin R^1 Wasserstoff ist, \underline{n} 1 oder 2 ist und R eine oder zwei der folgenden Bedeutungen hat:

Phenyl-, (C_1 - C_6 -Alkyl)phenyl-, Halogenphenyl-, Dihalogenphenyl-, Biphenyl-, (C_1 - C_5 -Alkoxy)phenyl-, Trihalogenmethylphenyl-, Nitrophenyl-, mit (C_1 - C_4 -Alkoxy)carbonylresten substituierter Phenyl-, Furanyl-, mit Ethylcarboxylat-, Cyano-, Chlor- oder Bromresten substituierter Furanyl-, Thienyl-, mit Ethylcarboxylat-, Cyano-, Chlor- oder Bromresten substituierter Thienyl- oder (C_1 - C_6 -Alkyl)nitrophenylrest ist.

6. Verfahren nach Anspruch 5, worin R^1 Wasserstoff ist, \underline{n} 1 oder 2 ist und R ein 4-Chlorphenyl-, 3-Nitrophenyl-, 3,4-Dichlorphenyl-, 3-Fluorphenyl-, 2-Thienyl-, 4-Methylphenyl-, 3-Trifluormethylphenyl-, 3-Ethanonphenyl-, 3,5-Dichlorphenyl-, 4-Trifluormethylphenyl- oder 3-Methyl-4-nitrophenylrest ist.

7. Verfahren nach Anspruch 4, worin R^1 Wasserstoff ist und R



ist, worin X Schwefel ist, Y Stickstoff oder -CH- ist und R'' Wasserstoff ist.

8. Verfahren nach Anspruch 4, worin 0,05 bis 0,4 kg/m^2 der Verbindung auf die Oberfläche von Holz oder Holzverbundmaterial aufgetragen werden.

9. Verfahren nach Anspruch 4, worin etwa 0,5 bis etwa 6,0 kg/m^3 der Verbindung auf das Holz oder das Holzver-

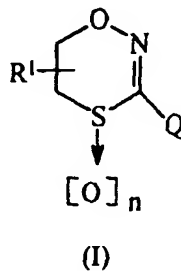
bundmaterial aufgetragen werden.

10. Zusammensetzung zur Konservierung von Holz oder Holzverbundmaterial umfassend

- a) eine wirksame Menge einer Verbindung nach Anspruch 1 und
b) einen geeigneten Träger.

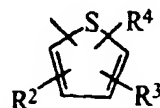
Revendications

1. Composé de la formule



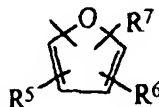
où n est 0, 1 ou 2 ; R_1 est hydrogène, alkyle C_1 - C_4 linéaire ou ramifié ou benzyle ; et Q est

(a)



où R^2 , R^3 et R^4 sont individuellement hydrogène, alkyle, alcoxy, alkylthio, alcoxycarbonyl, halogène, trihalométhyle, cyano, acétyle, formyle, benzoyl, nitro, alcoxyaminométhyle, phényle ou phénylaminocarbonyl, où les fragments alkyle ou alcoxy sont tous C_1 - C_4 , linéaires ou ramifiés à condition qu'au moins l'un de R^2 , R^3 ou R^4 doive être autre que de l'hydrogène ;

(b)



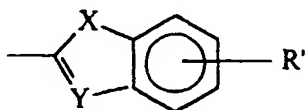
où R^5 , R^6 et R^7 sont individuellement, hydrogène, alcoxy C_1 - C_4 , alkylthio C_1 - C_4 , halogène, trihalométhyle, cyano, acétyle, formyle, benzoyl, nitro, phényle ou phénylaminocarbonyl, à condition qu'au moins l'un de R^5 , R^6 ou R^7 doive être autre qu'hydrogène ;

(c)



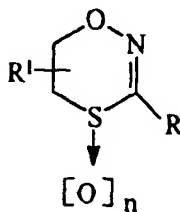
où R^8 , R^9 et R^{10} sont individuellement, hydroxyle, halo, alkyle C_1 - C_{12} , cycloalkyle C_5 - C_6 , trihalométhyle, phényle, alcoxy C_1 - C_5 , alkylthio C_1 - C_5 , tétrahydropyranyloxy, phénoxy, (alkyle C_1 - C_4)carbonyle, phénylcarbonyle, alkylsulfinyle C_1 - C_4 , alkylsulfonyl C_1 - C_4 , carboxy ou son sel d'un métal alcalin, (alcoxy C_1 - C_4)carbonyle, (alkyle C_1 - C_4) amino-carbonyle, phénylaminocarbonyle, tolylaminocarbonyle, morpholinocarbonyle, amino, nitro, cyano, dioxolanyle, ou alcoxy (C_1 - C_4) iminométhyle ; ou

(d)



où X est oxygène ou soufre ; Y est azote, $-CH-$, ou $-C(\text{alcoxy } C_1-C_4)-$; et R'' est hydrogène ou alkyle C_1 - C_4 .

2. Composé selon la revendication 1 où R^1 est hydrogène ou alkyle C_1 - C_4 ; n est 1 ou 2 ; R^2 , R^3 et R^4 sont individuellement hydrogène, alkyle C_1 - C_4 , halo, (alcoxy C_1 - C_4)-carbonyle ou cyano à condition qu'au moins l'un de R^2 , R^3 et R^4 doive être autre qu'hydrogène ; R^5 , R^6 et R^7 sont individuellement hydrogène, halo ou cyano, à condition qu'au moins l'un de R^5 , R^6 et R^7 doive être autre qu'hydrogène ; R^8 , R^9 , et R^{10} sont alkyle C_1 - C_4 , alcoxy C_1 - C_4 , nitro, halo, trihalométhyle, ou (alcoxy C_1 - C_4)-carbonyle ; X est soufre et R'' est hydrogène.
3. Composé selon la revendication 2 où R^1 est oxygène ; n est 1 ou 2 ; R^2 , R^3 , R^4 sont individuellement hydrogène, méthyle, éthyle, bromo, chloro, carboxylate d'éthyle ou cyano, à condition qu'au moins l'un de R^2 , R^3 et R^4 doive être autre qu'hydrogène ; R^5 , R^6 et R^7 sont individuellement hydrogène, bromo, chloro ou cyano, à condition qu'au moins l'un de R^5 , R^6 et R^7 doive être autre qu'hydrogène ; R^8 , R^9 et R^{10} sont méthyle, éthyle, nitro, fluoro, chloro ou trifluorométhyle.
4. Méthode pour préserver le bois ou un matériau de bois composite qui consiste à traiter le bois ou le matériau de bois composite avec une quantité fongicidement ou bactéricidement efficace d'un composé de la formule



(II)

où n est 0 ou 1 ; R^1 est hydrogène, alkyle C_1 - C_4 linéaire ou ramifié ou benzyle ; et R est

(a) phényle ; naphthyle ; phényle substitué par 1-3 des substituants suivants :

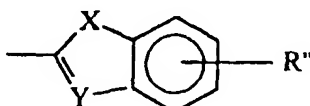
hydroxyle, halo, alkyle C₁-C₁₂, cycloalkyle C₅-C₆, trihalométhyle, phényle, alcoxy C₁-C₅, alkylthio C₁-C₅, tétrahydropyranyloxy, phénoxy, (alkyl C₁-C₄)carbonyle, phénylcarbonyle, alkylsufinyle C₁-C₄, alkylsulfonyle C₁-C₄, carboxy ou son sel d'un métal alcalin, (alcoxy C₁-C₄)carbonyle, (alkyle C₁-C₄)aminocarbonyle, phénylaminocarbonyle, toylaminocarbonyle, morpholinocarbonyle, amino, nitro, cyano, dioxolanyle, ou (alcoxy C₁-C₄)-iminométhyle ;

pyridinyle ; thiényle, furanyle ; thienyl ou furanyl substitué par 1 à 3 des groupes suivants :

alkyle, alcoxy, alkylthio, alcoxycarbonyle, halogène, trihalométhyle, cyano, acétyle, formyle, benzoyle, nitro, phényle ou phénylaminocarbonyle, ou le fragment alkyle ou alcoxy est C₁-C₄, linéaire ou ramifié ;

ou bien thiényle substitué par 1 à 3 alcoxyaminométhyles où le fragment alcoxy est C₁-C₄, linéaire ou ramifié ; ou

(b)

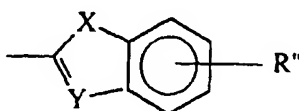


où X est oxygène ou soufre ; Y est azote, -CH-, ou -C(alcoxy C₁-C₄)- ; et R'' est hydrogène ou alkyle C₁-C₄.

5. Méthode selon la revendication 4 où R¹ est hydrogène, n est un ou deux, et R a une ou deux des valeurs suivantes : phényle, (alkyl C₁-C₆)phényle, halophényle, dialophényle, biphényle, (alkyloxy C₁-C₅)phényle, trihalométhylphényle, nitrophényle, phényle substitué par (alcoxy C₁-C₄)carbonyle, furanyle, furanyle substitué par du du carboxylate d'éthyle, cyano, chlore ou brome, thiényle, thiényle substitué par du carboxylate d'éthyle, cyano, chlore ou brome ou (alkyl C₁-C₆) nitrophényle.

6. Méthode selon la revendication 5 où R¹ est hydrogène, n est un ou deux et R est représenté par : 4-chlorophényle, 3-nitrophényle, 3,4-dichlorophényle, 3-fluorophényle, 2-thiényle, 4-méthylphényle, 3-trifluorométhyle, 3-éthanone phényle, 3,5-dichlorophényle, 4-trifluorométhylphényle ou 3-méthyl-4-nitrophényle.

7. Méthode selon la revendication 4 où R¹ est hydrogène et R est



où X est soufre, Y est azote ou -CH-, et R'' est hydrogène.

8. Méthode selon la revendication 4 où on applique entre environ 0,05 et 0,4 kg/m² du composé à l'aire superficielle du bois ou du matériau de bois composite.

9. Méthode selon la revendication 4 où on applique environ 0,5 à environ 6,0 kg/m³ du composé dans le bois ou le matériau de bois composite.

10. Composition pour préserver le bois ou un matériau de bois composite qui comprend :

- a) une quantité efficace d'un composé selon la revendication 1 ; et
- b) un support approprié.